

Identification of Gas Chromatographic Effluents Through the Effect of Temperature on the Slope of a Log Retention Volume-Carbon Number Plot

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Abstract

A method is presented which extends the technique of using retention volume constants for qualitative functional group identification. The method involves systematic prediction of column operating temperatures to ensure that the slopes of log retention volume-carbon number plots on two columns are equal.

Introduction

Gas-liquid chromatography has become a powerful tool for the separation of mixtures of volatile compounds; however, its use has been handicapped by the lack of a positive means of identification of the separated compounds. Since many different components can have the same retention volume, it is necessary to use auxiliary methods of analysis, such as mass spectrometry or chemical reagent tests, to permit unambiguous identification of gas chromatographic effluents. An identification system based solely on gas chromatographic measurements would be of immense practical value. Such a system was proposed by Merritt and Walsh (1) more than 15 years ago. Their method employs two columns having different stationary phases. If the slopes of the log retention volume-carbon number plots for any given homologous series are the same on both stationary phases, then the retention volume of any compound within the given homologous series on one column divided by the retention volume of that same compound on the other column is constant. If it is also true that different chemical families display a retention volume constant unique to their own functionality, then it is possible to identify the functional group of a gas chromatographic peak.

The Merritt-Walsh system of identification by means of retention volume constants holds great promise for the practicing chromatographer, but it has not gained widespread acceptance. The reason for this is that it is difficult to find a pair of stationary phases which satisfy the two criteria essential to positive identification. These criteria are: (a) that any specified homologous series have the same slope of a log retention volume-carbon number plot on both stationary phases and (b) that different homologous series display different retention volume ratios. Of the 28 pairs of columns tested by Merritt and Walsh (1) only one pair, Carbowax 400 and Carbowax 20M, was judged to give very good functional group identification for the eight functional groups studied. This paper discusses a method whereby it is possible to predict operating conditions such that the first criterion above is more

often realized. That is, a method is presented that enables log retention volume-carbon number plots on different columns that originally were not parallel to be made parallel.

Thermodynamic Background

Consider two members of a homologous series at a specified temperature—one containing n_j carbon atoms and the other containing n_i carbon atoms. The slope, m_i , of the log retention volume-carbon number plot can be represented by:

$$m_i = \frac{\ln V_g(n_j) - \ln V_g(n_i)}{n_j - n_i} \quad (1)$$

where $V_g(n_j)$ denotes the value of the specific retention volume of the compound containing n_j carbon atoms. The specific retention volume can be written as (2):

$$V_g = \frac{273R}{\gamma_2^\infty M_1 f_2^\infty} \quad (2)$$

where R is the gas constant, γ_2^∞ is the activity coefficient of the solute at infinite dilution in the stationary phase (the standard state is taken to be pure solute at the same temperature and pressure as that of the solution), M_1 is the molecular weight of the solvent (stationary phase), and f_2^∞ is the fugacity of the pure solute at the temperature and pressure of the solution. The fugacity, f_2^∞ , can be replaced by the pure-solute vapor pressure at the temperature of interest with little error in most cases.

The temperature derivatives of the activity coefficient and the pure-component fugacity are given by the exact thermodynamic relations (3) and (4).

$$\left(\frac{\partial \ln \gamma_2^\infty}{\partial 1/T} \right)_p = \frac{(h_2^* - h_2^\infty)}{R} \quad (3)$$

$$\left(\frac{\partial \ln f_2^\infty}{\partial 1/T} \right)_p = \frac{(\bar{h}_2^\infty - h_2)}{R} \quad (4)$$

where h_2 is the enthalpy of pure solute, h_2^* is the enthalpy of pure solute in the ideal-gas state, and \bar{h}_2^∞ is the partial molar enthalpy of the solute at infinite dilution in the stationary phase.

From the above relations it follows that:

$$\frac{d \ln V_g}{d(1/T)} = \frac{(h_2^* - h_2^\infty)}{R} = \frac{\Delta H_2^\infty}{R} \quad (5)$$

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where ΔH_e^S represents the enthalpy of evaporation of the solute from the infinite-dilution solution. Differentiating equation 1 with respect to inverse temperature and substituting from equation 5 yields:

$$\frac{dm}{d(1/T)} = \frac{1}{R} \left[\frac{\Delta H_e^S(n_j) - \Delta H_e^S(n_i)}{n_j - n_i} \right] \quad (6)$$

It is reasonable to expect that the addition of successive $-CH_2-$ units to members of a homologous series should produce constant increments in ΔH_e^S . In this case the right-hand side of equation 6 multiplied by R represents the differential molar enthalpy of evaporation of a methylene group from solution, $\Delta H_e^S(CH_2)$. Risby et al. (4,5) have employed equation 6 to calculate values of $\Delta H_e^S(CH_2)$ using data from 7 homologous series on 75 liquid phases. They use these values in a method for predicting specific retention volumes and characterizing stationary phases.

The purpose of the present work is not to emphasize differences in solution behavior and generate tables of thermodynamic parameters, but rather to exploit the remarkable generality of equation 6. To a first approximation, this equation predicts that the change in slope of a log retention volume-carbon number plot with respect to inverse temperature is constant, regardless of the chemical family chosen as solute and the stationary phase chosen as solvent. This constant will be universal for all solute-solvent systems to the extent that the right-hand side of equation 6 is independent of the functional groups contained in the solute and the solvent. To this effect equation 6 is written as:

$$\frac{dm}{d(1/T)} = k \quad (7)$$

where k is a constant. If a value of k can be found, which is indeed constant irrespective of solute-solvent system, then equation 7 can be used to predict the change in temperature that is necessary to yield parallel plots of log retention volume vs. carbon number for a homologous series on two different stationary phases. This should increase the number of column pairs that can be employed in the Merritt-Walsh system of qualitative identification by means of retention volume constants.

Data Reduction

To provide a large, statistically significant data base, the compilation of gas chromatographic retention data by McReynolds (6) was used. A computer program was written which accepted as input the specific retention volume values of a family of compounds and calculated the slope and intercept of the log retention volume-carbon number plot by the least squares method. Data were obtained in this way for 8 homologous series on 75 stationary phases. The families and respective compounds used in evaluation were: alcohols (C_2-C_9), aldehydes (C_2-C_7), 2-ketones (C_3-C_9), formates (C_1-C_6), acetates (C_1-C_7), propionates (C_1-C_5), butyrates (C_1-C_5), and n -alkanes (C_4-C_{16}).

The relative uncertainty of the literature data was at most one-tenth unit in every 100 units, for a percentage precision of 0.1. The percentage precision in the slope values was thus no greater than 0.1 and these numbers were rounded to three significant figures.

Each family on each column was run at two temperatures so that the differences in the slopes of the log retention volume-

carbon number plots at different temperatures could be used to approximate the derivative in equation 7. The mean value of k was $\bar{k} = 416$, with a standard deviation of 87. The distribution of k values is presented in histogram form in Figure 1. The k values are based on the use of logarithms of base e (natural logarithms).

The value k in this work corresponds to the quantity $\Delta H_e^S(CH_2)/R$ used by Risby et al. (4). Table V of Risby et al. (4) lists values of $\Delta H_e^S(CH_2)$ for the stationary phases used by McReynolds (6) and the following families: alkanes, alkanols, alkanals, alkanones, formates, acetates, and ethers. Using these data yields $\bar{k} = 417 \pm 87$.

Applications

Merritt et al. (7) and McCarthy et al. (8) found that log retention volume-carbon number plots of a homologous series on two stationary phases that were not parallel when the two columns were operated at the same temperature could be made parallel by operating one of the columns at a different temperature. In particular, McCarthy et al. (8) used a Carbowax 4000 column at 72°C and a UCON polar column at 92°C to identify banana fruit volatiles. This successful column combination was arrived at through laboratory trial and error. Such guesswork can be eliminated by using equation 7. To demonstrate, Table I lists the values of the slopes of log retention volume carbon-number plots at 100°C for 5 families on the two columns, UCON 50 HB-2000 and Carbowax 1540. The data were obtained from McReynolds (6); Carbowax 4000 could not be used since data were not available at 100°C for comparison with UCON polar. It is evident from Table I that an average change of 0.085 in the slopes of the lines on the Carbowax column is necessary to make the respective homologous series parallel to those on the UCON column. Thus:

$$\Delta m = 0.085 = k\Delta(1/T) - 416 \left(\frac{1}{T} - \frac{1}{373} \right)$$

which has the solution $T = 73^\circ\text{C}$. The slopes of homologous-series lines on Carbowax 1540 at 73°C were predicted by extrapolation of $\log V_g$ vs. $1/T$ plots, and the results are shown in Table II. A difference of less than 0.02 units in slope values is not discernible on semi-logarithmic graph paper and is within the accuracy of the retention values themselves. The log retention volume-carbon number plots are now parallel and are acceptable for the calculation of retention volume constants and the identification of gas chromatographic effluents.

78% of the k values in Figure 1 are in the range of $\bar{k} \pm (1 \text{ standard deviation})$. If the smallest and largest k values in this range were used in the preceding calculation the predicted temperature would have been 67 and 78°C, respectively. Operating the Carbowax column at any temperature from 70 to 76°C gives log retention volume-carbon number plots whose slopes differ by less than 0.02. Of course, the optimum value of k for a given stationary phase, homologous series, and temperature range could be used for calculation; however, the generality and simplicity of the method described above may be lost in a plethora of empirical constants.

Conclusion

In a simple manner, then, it is possible to predict the change in temperature required to effect a particular change in the slope of a log retention volume-carbon number plot. The change in slope varies directly with the change in inverse tem-

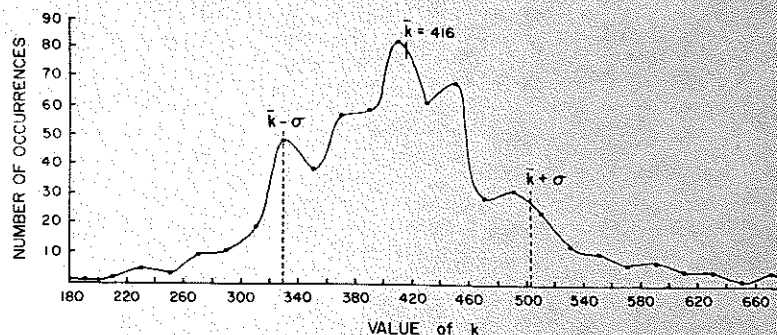


Figure 1. Distribution of values of the slope 1 temperature constant (Equation 7) computed from a library of retention data.

Table I. Slopes of Log Retention Volume-Carbon Number Plots

Family	UCON 50 HB-2000, 100°C	Carbowax 1540, 100°C	Δm
1-alcohols	0.688	0.617	0.071
aldehydes	0.700	0.587	0.113
acetates	0.640	0.555	0.085
butyrates	0.580	0.504	0.076
2-ketones	0.645	0.564	0.081
			$\Delta m = 0.085$

Table II. Slopes of Log Retention Volume-Carbon Number Plots.

Family	Carbowax 1540, 73°C
1-alcohols	0.700
aldehydes	0.668
acetates	0.636
butyrates	0.592
2-ketones	0.647

perature, and the proportionality constant can be assumed independent of chemical family and stationary phase. This assumption is well suited for use in the determination of parallel column plots in the Merritt-Walsh scheme of identification by means of retention volume constants.

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References

1. C. Merritt, Jr. and J.T. Walsh. Qualitative gas chromatographic analysis by means of retention volume constants. *Anal. Chem.* **34**: 903 (1962).
2. A.B. Littlewood. *Gas Chromatography—Principles, Techniques, and Applications*. Academic Press, New York, 1970.
3. J.M. Prausnitz. *Molecular Thermodynamics of Fluid-Phase Equilibria*. Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1969.
4. T.H. Risby, P.C. Jurs, and B.L. Reinbold. Use of thermodynamic solubility parameters for the characterization of liquid phases. *J. Chromatogr.* **99**: 173 (1974).
5. C.E. Figgins, T.H. Risby, and P.C. Jurs. The use of partial molal entropies and free energies in the characterization of gas chromatographic stationary phases. *J. Chromatogr. Sci.* **14**: 453 (1976).
6. W.O. McReynolds. *Gas Chromatographic Retention Data*. Preston Technical Abstracts Co., Evanston, Illinois 1966.
7. C. Merritt, Jr., J.T. Walsh, D.H. Robertson, and A.I. McCarthy. Qualitative gas chromatographic analysis by means of retention volume constants—behavior of isomers. *J. Gas Chromatogr.* **2**: 125 (1964).
8. A. McCarthy, H. Wyman, and J.K. Palmer. Gas chromatographic identification of banana fruit volatiles. *J. Gas Chromatogr.* **2**: 121 (1964).

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